

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
22 July 2004 (22.07.2004)

PCT

(10) International Publication Number
WO 2004/061909 A1

(51) International Patent Classification⁷: **H01L 21/00**

(74) Agent: GATES, George, H.; Gates & Cooper LLP, 6701 Center Drive West, Suite 1050, Los Angeles, CA 90045 (US).

(21) International Application Number:
PCT/US2003/021918

(22) International Filing Date: 15 July 2003 (15.07.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/433,843 16 December 2002 (16.12.2002) US
60/433,844 16 December 2002 (16.12.2002) US

(71) Applicant (for all designated States except US): **THE REGENTS OF THE UNIVERSITY OF CALIFORNIA** [US/US]; 1111 Franklin Street, 12th Floor, Oakland, CA 94607 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **HASKELL, Benjamin, A.** [US/US]; 724 Kroeber Walk, #207, Goleta, CA 93117 (US). **CRAVEN, Michael, D.** [US/US]; 68 1/2 Deerhurst Drive, Goleta, CA 93117 (US). **FINI, Paul, T.** [US/US]; 218 West Mason Street, Santa Barbara, CA 93101 (US). **DENBAARS, Steven, P.** [US/US]; 287 King Daniel Lane, Goleta, CA 93117 (US). **SPECK, James, S.** [US/US]; 947 West Campus Lane, Goleta, CA 93117 (US). **NAKAMURA, Shuji** [JP/US]; 4517 Vieja Drive, Santa Barbara, CA 93110 (US).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declaration under Rule 4.17:

— of inventorship (Rule 4.17(iv)) for US only

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

BEST AVAILABLE COPY

WO 2004/061909 A1

(54) Title: GROWTH OF REDUCED DISLOCATION DENSITY NON-POLAR GALLIUM NITRIDE BY HYDRIDE VAPOR PHASE EPITAXY

(57) Abstract: Lateral epitaxial overgrowth (LEO) of non-polar a-plane gallium nitride (GaN) films by hydride vapor phase epitaxy (HVPE) results in significantly reduced defect density.

GROWTH OF REDUCED DISLOCATION DENSITY NON-POLAR GALLIUM
NITRIDE BY HYDRIDE VAPOR PHASE EPITAXY

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims priority to the following co-pending and commonly-assigned United States Provisional Patent Applications:

Serial No. 60/433,843, entitled "GROWTH OF REDUCED DISLOCATION
5 DENSITY NON-POLAR GALLIUM NITRIDE BY HYDRIDE VAPOR PHASE
EPITAXY," filed on December 16, 2002, by Benjamin A. Haskell, Michael D.
Craven, Paul T. Fini, Steven P. DenBaars, James S. Speck, and Shuji Nakamura,
attorneys docket number 30794.93-US-P1; and

Serial No. 60/433,844, entitled "TECHNIQUE FOR THE GROWTH OF
10 PLANAR, NON-POLAR A-PLANE GALLIUM NITRIDE BY HYDRIDE VAPOR
PHASE EPITAXY," filed on December 16, 2002, by Benjamin A. Haskell, Paul T.
Fini, Shigemasa Matsuda, Michael D. Craven, Steven P. DenBaars, James S. Speck,
and Shuji Nakamura, attorneys docket number 30794.94-US-P1;

both of which applications are incorporated by reference herein.

15 This application is related to co-pending and commonly-assigned International
Application No. PCT/US03/-----, entitled "GROWTH OF PLANAR, NON-POLAR
A-PLANE GALLIUM NITRIDE BY HYDRIDE VAPOR PHASE EPITAXY," filed
on same date herewith, by Benjamin A. Haskell, Paul T. Fini, Shigemasa Matsuda,
Michael D. Craven, Steven P. DenBaars, James S. Speck, and Shuji Nakamura,
20 attorneys docket number 30794.94-WO-U1, which application claims priority to co-
pending and commonly-assigned United States Provisional Patent Application Serial
No. 60/433,844, entitled "TECHNIQUE FOR THE GROWTH OF PLANAR, NON-
POLAR A-PLANE GALLIUM NITRIDE BY HYDRIDE VAPOR PHASE
EPITAXY," filed on December 16, 2002, by Benjamin A. Haskell, Paul T. Fini,
25 Shigemasa Matsuda, Michael D. Craven, Steven P. DenBaars, James S. Speck, and
Shuji Nakamura, attorneys docket number 30794.94-US-P1; and United States

Provisional Patent Application Serial No. 60/433,843, entitled "GROWTH OF REDUCED DISLOCATION DENSITY NON-POLAR GALLIUM NITRIDE BY HYDRIDE VAPOR PHASE EPITAXY," filed on December 16, 2002, by Benjamin A. Haskell, Michael D. Craven, Paul T. Fini, Steven P. DenBaars, James S. Speck, and Shuji Nakamura, attorneys docket number 30794.93-US-P1; which applications are incorporated by reference herein.

1. Field of the Invention.

The invention is related to semiconductor materials, methods, and devices, and more particularly, to the growth of reduced dislocation density non-polar gallium nitride (GaN) by hydride vapor phase epitaxy (HVPE).

2. Description of the Related Art.

(Note: This application references a number of different patents, applications and/or publications as indicated throughout the specification by one or more reference numbers. A list of these different publications ordered according to these reference numbers can be found below in the section entitled "References." Each of these publications is incorporated by reference herein.)

The usefulness of gallium nitride (GaN) and its ternary and quaternary compounds incorporating aluminum and indium (AlGaN, InGaN, AlInGaN) has been well-established for fabrication of visible and ultraviolet optoelectronic devices and high-power electronic devices. (See References 1-3.) These devices are typically grown epitaxially, layer by layer oriented to a substrate, by growth techniques including molecular beam epitaxy (MBE), metalorganic chemical vapor deposition (MOCVD), or hydride vapor phase epitaxy (HVPE).

GaN and its alloys are most stable in the hexagonal wurtzite crystal structure, in which the crystal is described by two (or three) equivalent basal plane axes that are rotated 120° with respect to each other (the a-axes), all of which are perpendicular to a unique c-axis. FIG. 1 is a schematic of a generic hexagonal wurtzite crystal structure

100 and planes of interest 102, 104, 106, 108 with these axes 110, 112, 114, 116 identified therein.

As a consequence of the gallium and nitrogen atom positions within the würtzite crystal structure 100, any plane of atoms lying perpendicular to the c-axis will contain only one type of atom. As one proceeds from plane to plane along the c-axis, each plane will contain only one type of atoms, either Ga or N. In order to maintain charge neutrality, GaN crystals terminate with one c-face that contains only nitrogen atoms (the N-face), and one c-face that only contains gallium atoms (the Ga-face). As a consequence, GaN crystals are polarized along the c-axis. The spontaneous polarization of these crystals is a bulk property and depends on the structure and composition of the crystal.

Due to the relative ease of growing planar Ga-face c-planes, virtually all GaN-based devices are grown parallel to the polar c-axis. A negative consequence of this growth direction is that each layer material will suffer from segregation of electrons and holes to opposite faces of the layers due to the spontaneous polarization of the crystal. Furthermore, strain at the interfaces between adjacent layers gives rise to piezoelectric polarization, causing further charge separation within quantum heterostructures. Such polarization effects decrease the likelihood that electrons and holes will interact, a necessity for the operation of light-emitting optoelectronic devices. It is believed that the efficiency of GaN light-emitting devices would be enhanced were it possible to eliminate the polarization effects inherent to c-axis oriented devices.

One possible approach to eliminating the piezoelectric polarization effects in GaN optoelectronic devices is to grow the devices on non-polar planes of the crystal. (See References 4-6.) Such planes contain equal numbers of Ga and N atoms and are charge-neutral. Furthermore, subsequent non-polar layers are equivalent to one another so the bulk crystal will not be polarized along the growth direction. One such family of symmetry-equivalent non-polar planes in GaN is the $\{11\bar{2}0\}$ family, known collectively as a-planes. Growth on electronic devices, such as high electron mobility

transistors; or optoelectronic devices, such as visible and ultraviolet laser diodes and light-emitting diodes; on *a*-plane substrates could yield significantly enhanced device performance compared to equivalent devices grown on *c*-plane GaN.

Bulk crystals of GaN are not available so it is not possible to simply cut a
5 crystal to present a surface for subsequent device regrowth. All GaN films are initially grown heteroepitaxially, i.e. on foreign substrates that provide a reasonable lattice match to GaN. In recent years, a number of research groups have found it possible to utilize HVPE as a means of heteroepitaxially depositing *c*-plane GaN films that are thick enough ($>200\text{ }\mu\text{m}$) to remove the foreign substrate, yielding a free-standing GaN
10 substrate that may then be used for homoepitaxial device regrowth by MBE and MOCVD. (See References 7-8.)

HVPE has the advantage of growth rates that are one to two orders of magnitude greater than that of MOCVD and as many as three orders of magnitude greater than MBE, an advantage that makes it an attractive technique for substrate
15 fabrication.

The growth of planar *a*-plane GaN by HVPE has recently been demonstrated, as described in the co-pending and commonly-assigned International Application No. PCT/US03/-----, entitled "GROWTH OF PLANAR, NON-POLAR A-PLANE GALLIUM NITRIDE BY HYDRIDE VAPOR PHASE EPITAXY," filed on same
20 date herewith, by Benjamin A. Haskell, Paul T. Fini, Shigemasa Matsuda, Michael D. Craven, Steven P. DenBaars, James S. Speck, and Shuji Nakamura, attorneys docket number 30794.94-WO-U1, which application claims priority to co-pending and commonly-assigned United States Provisional Patent Application Serial No. 60/433,844, entitled "TECHNIQUE FOR THE GROWTH OF PLANAR, NON-
25 POLAR A-PLANE GALLIUM NITRIDE BY HYDRIDE VAPOR PHASE EPITAXY," filed on December 16, 2002, by Benjamin A. Haskell, Paul T. Fini, Shigemasa Matsuda, Michael D. Craven, Steven P. DenBaars, James S. Speck, and Shuji Nakamura, attorneys docket number 30794.94-US-P1; and United States Provisional Patent Application Serial No. 60/433,843, entitled "GROWTH OF

REDUCED DISLOCATION DENSITY NON-POLAR GALLIUM NITRIDE BY
HYDRIDE VAPOR PHASE EPITAXY," filed on December 16, 2002, by Benjamin
A. Haskell, Michael D. Craven, Paul T. Fini, Steven P. DenBaars, James S. Speck,
and Shuji Nakamura, attorneys docket number 30794.93-US-P1; which applications
5 are incorporated by reference herein. (See References 9-10.)

While this work represents an enabling technology for the growth of non-polar
GaN devices, the relatively high defect density in the directly-grown a-GaN films
reduces the efficiency of subsequently grown devices compared to what could be
achieved by homoepitaxial growth on a perfect substrate. There is an ever-increasing
10 effort to reduce the dislocation density in GaN films in order to improve device
performance.

The two predominant types of extended defects of concern are threading
dislocations and stacking faults. The primary means of achieving reduced dislocation
and stacking fault densities in polar c-plane GaN films is the use of a variety of lateral
15 overgrowth techniques, including lateral epitaxial overgrowth (LEO, ELO, or ELOG),
selective area epitaxy, and PENDEO® epitaxy. The essence of these processes is to
block or discourage dislocations from propagating perpendicular to the film surface
by favoring lateral growth over vertical growth. These dislocation-reduction
techniques have been extensively developed for c-plane GaN growth by HVPE and
20 MOCVD. (See References 11-18.)

Only recently have GaN lateral growth techniques been demonstrated for a-
plane films. Craven, et al., succeeded in performing LEO using a dielectric mask on a
thin a-plane GaN template layer via MOCVD. (See Reference 19.)

However, HVPE-based LEO of a-plane GaN has not previously been
25 accomplished. Thus, there is a need in the art for methods of growing high-quality,
low-defect density, non-polar, a-plane $\{11\bar{2}0\}$ GaN films. More specifically, there is a
need in the art for methods of growing such GaN films using lateral overgrowth by
HVPE. The present invention satisfies this need.

SUMMARY OF THE INVENTION

The present invention discloses a method of performing a lateral epitaxial overgrowth of a planar, non-polar, a-plane GaN film, comprising: (a) patterning a mask deposited on a substrate; and (b) performing a lateral epitaxial overgrowth of the GaN film off the substrate using hydride vapor phase epitaxy, wherein the GaN film nucleates only on portions of the substrate not covered by the patterned mask, the GaN film grows vertically through openings in the patterned mask, and the GaN film then spreads laterally above the patterned mask and across the substrate's surface. The lateral epitaxial overgrowth reduces threading dislocation densities in the GaN film.

BRIEF DESCRIPTION OF THE DRAWINGS

Referring now to the drawings in which like reference numbers represent corresponding parts throughout:

FIG. 1 is a schematic of a generic hexagonal würtzite crystal structure and planes of interest with these axes identified therein;

FIG. 2 is a flowchart that illustrates a method of performing a lateral epitaxial overgrowth of a planar, non-polar, a-plane gallium nitride (GaN) film according to the preferred embodiment of the present invention;

FIG. 3 is a cross-sectional scanning electron micrograph (SEM) image of an a-plane GaN stripe;

FIG. 4(a) is a schematic representation of a $[1\bar{1}00]$ stripe geometry;

FIG. 4(b) is an optical contrast micrograph of a 20 μm -thick coalesced LEO film formed with $[1\bar{1}00]$ -oriented stripes;

FIG. 4(c) is a 10 x 10 μm atomic force micrography topograph of two coalesced stripes;

FIG. 5(a) and (b) are cross-sectional SEM images of LEO wafers patterned with a periodic array of $[1\bar{1}00]_{\text{GaN}}$ - oriented SiO_2 stripes;

FIG. 5(c) is a plan-view SEM image of a coalesced film;

FIG. 5(d) is a cathodoluminescence (CL) image of a coalesced film; and
FIGS. 6(a), (b) and (c) show plan-view and cross-sectional TEM images of a
LEO film imaged with g vectors of $1\bar{1}00$ and $01\bar{1}0$.

5

DETAILED DESCRIPTION OF THE INVENTION

In the following description of the preferred embodiment, reference is made to
the accompanying drawings which form a part hereof, and in which is shown by way
of illustration a specific embodiment in which the invention may be practiced. It is to
be understood that other embodiments may be utilized and structural changes may be
made without departing from the scope of the present invention.

10

Overview

The present invention reduces threading dislocation densities in HVPE-grown
non-polar, a-plane GaN films using LEO. By utilizing reduced growth pressures and a
carrier gas containing a fraction of hydrogen, lateral growth of a non-polar GaN film
directly off a foreign substrate can be achieved. A patterned mask is applied to the
substrate through one of a variety of means. The substrate is then loaded into a HVPE
reactor and the a-GaN film grows only from the regions of exposed substrate material
and spreads laterally above the mask and across the substrate surface.

15

The present invention allows significant defect reduction and film quality
improvement, as compared to non-polar GaN films grown directly on uniform
substrates. Such reduced defect density non-polar GaN films will provide for
improvements in the electronic, optoelectronic, and electromechanical devices that are
subsequently grown on the template films grown by this technique. Moreover, the
laterally overgrown films described herein further provide an excellent means of
reducing the dislocation density in thick non-polar GaN films that can be debonded to
form free-standing substrates.

20

25

The preferred embodiment of the present invention for dislocation reduction
includes:

1. Use of a patterned substrate, such as an r-plane sapphire (Al_2O_3) substrate with a silicon dioxide (SiO_2) mask containing apertures or stripes therein allowing access to the underlying sapphire substrate.
2. Growth of a non-polar GaN film under conditions that yield planar
5 non-polar GaN films on the sapphire substrate.

Process Steps

FIG. 2 is a flowchart that illustrates a method of performing a lateral epitaxial overgrowth of a planar, non-polar, a-plane GaN film according to the preferred
10 embodiment of the present invention. These steps comprise patterning a mask deposited on a substrate (Blocks 200-208 below), and performing a lateral epitaxial overgrowth of the GaN film off the substrate using hydride vapor phase epitaxy (Blocks 210-224 below), wherein the GaN film nucleates only on portions of the substrate not covered by the patterned mask, the GaN film grows vertically through
15 openings in the patterned mask, and the GaN film then spreads laterally above the patterned mask and across the substrate's surface.

Block 200 represents the step of depositing a 1300 Å-thick SiO_2 film on a 430 μm thick polished r-plane ($1\bar{1}02$) sapphire substrate, wherein the SiO_2 film provides the basis for the dielectric mask. Although, in the preferred embodiment, the
20 patterned mask is a dielectric, and the substrate is an r-plane sapphire substrate, other materials may be used as well, such as a metallic material for the patterned mask or silicon carbide (SiC) for the substrate.

Block 202 represents the step of depositing a photoresist layer on the SiO_2 film and patterning the deposited photoresist layer using conventional
25 photolithography processing steps. In one embodiment, the pattern comprises 35 μm wide stripes separated by 5 μm wide openings.

Block 204 represents the step of etching away any portions of the SiO_2 film exposed by the patterned photoresist layer by soaking the substrate in buffered hydrofluoric (HF) acid for two minutes.

Block 206 represents the step of removing remaining portions of the photoresist layer using acetone.

Block 208 represents the step of cleaning the substrate using acetone, isopropyl alcohol, and deionized water.

5 After drying, the substrate is covered by a patterned mask comprising the patterned SiO₂ film having 35 μm wide stripes separated by 5 μm wide openings.

The following Blocks represent the steps of performing a lateral epitaxial overgrowth of the GaN film off the substrate using HVPE, wherein the GaN film nucleates only on portions of the substrate exposed by the patterned mask, the GaN
10 film grows vertically through openings in the patterned mask, and the GaN film then spreads laterally above the patterned mask and across the substrate's surface, eventually converging with adjacent GaN stripes. The lateral epitaxial overgrowth utilizes reduced growth pressures of approximately atmospheric pressure (760 Torr) and a carrier gas containing a fraction of hydrogen.

15 These steps, and the growth parameters therefor, are described in more detail in the co-pending and commonly-assigned International Application No. PCT/US03/-----, entitled "GROWTH OF PLANAR, NON-POLAR A-PLANE GALLIUM NITRIDE BY HYDRIDE VAPOR PHASE EPITAXY," filed on same date herewith, by Benjamin A. Haskell, Paul T. Fini, Shigemasa Matsuda, Michael D.
20 Craven, Steven P. DenBaars, James S. Speck, and Shuji Nakamura, attorneys docket number 30794.94-WO-U1, which application claims priority to co-pending and commonly-assigned United States Provisional Patent Application Serial No. 60/433,844, entitled "TECHNIQUE FOR THE GROWTH OF PLANAR, NON-POLAR A-PLANE GALLIUM NITRIDE BY HYDRIDE VAPOR PHASE
25 EPITAXY," filed on December 16, 2002, by Benjamin A. Haskell, Paul T. Fini, Shigemasa Matsuda, Michael D. Craven, Steven P. DenBaars, James S. Speck, and Shuji Nakamura, attorneys docket number 30794.94-US-P1; and United States Provisional Patent Application Serial No. 60/433,843, entitled "GROWTH OF REDUCED DISLOCATION DENSITY NON-POLAR GALLIUM NITRIDE BY

HYDRIDE VAPOR PHASE EPITAXY," filed on December 16, 2002, by Benjamin A. Haskell, Michael D. Craven, Paul T. Fini, Steven P. DenBaars, James S. Speck, and Shuji Nakamura, attorneys docket number 30794.93-US-P1; which applications are incorporated by reference herein. See also References 9-10.

5 Block 210 represents the step of loading the substrate into a reactor.

Block 212 represents the step of evacuating the reactor and backfilling the reactor with purified nitrogen (N_2) gas to reduce oxygen levels therein. This step is frequently repeated to further reduce residual oxygen levels within the reactor.

10 Block 214 represents the step of heating the reactor to a growth temperature of approximately 1040°C , with a mixture of H_2 and N_2 flowing through all channels in the system.

15 Block 216 represents the step of nitridating the sapphire substrate, once the reactor reaches the growth temperature, wherein the nitridating step comprises adding anhydrous ammonia (NH_3) to a gas stream in the reactor to nitridate the surface of the sapphire substrate.

20 Block 218 represents the step of reducing the reactor's pressure to a desired deposition pressure. In the preferred embodiment, the desired deposition pressure is below atmospheric pressure (760 Torr), and is generally less than 300 Torr. More specifically, the desired deposition pressure may be restricted to a range of 5-100 Torr, and may be set to 76 Torr.

25 Block 220 represents the step of initiating a gaseous hydrogen chloride (HCl) flow to a gallium (Ga) source to begin growth of the a-plane GaN film directly on the sapphire substrate without the use of any low-temperature buffer or nucleation layers. Conventional metal source HVPE involves an in situ reaction of a halide compound, such as (but not limited to), gaseous HCl with the metallic Ga at a temperature in excess of 700°C to form gallium monochloride (GaCl).

Block 222 represents the step of transporting the GaCl to the substrate by a carrier gas that includes at least a fraction of hydrogen (H_2) in one or more of the gas streams in the reactor. In one embodiment, the carrier gas may be predominately

hydrogen, while in other embodiments the carrier gas comprises a mixture of hydrogen and nitrogen, argon, helium or other inert gases. Either in transport to the substrate, at the substrate, or in an exhaust stream, the GaCl reacts with the NH₃ to form the GaN film. Reactions that occur at the substrate have the potential to yield the GaN film on the substrate, thereby resulting in crystal growth. Typical V/III ratios are 1-50 for this process. Note that the NH₃/HCl ratio need not equal the V/III ratio due to supplemental HCl injection downstream of the Ga source or incomplete reaction of HCl with the Ga source.

Block 224 represents, after a desired growth time has elapsed, the step of interrupting the gaseous HCl flow, reducing the reactor's temperature to room temperature, and returning the reactor pressure to atmospheric pressure. The system pressure may be either atmospheric or reduced during this cooling phase. The interrupting step further comprises including NH₃ in a gas stream to prevent decomposition of the GaN film during the reduction of the reactor's temperature.

Preferably, the above process steps create a lateral epitaxial overgrowth of a planar, non-polar, a-plane gallium nitride (GaN) film off the substrate. Moreover, the above process steps are used to manufacture a free-standing a-plane GaN film or substrate. Devices manufactured using this method include laser diodes, light-emitting diodes and transistors.

Experimental Results

In experiments by the inventors, a variety of dielectric mask patterns were used to produce 8-125 μm -thick, fully coalesced non-polar GaN films. The nanometer-scale pit densities in the overgrown regions were less than $3 \times 10^6 \text{ cm}^{-2}$ as compared to $\sim 10^{10} \text{ cm}^{-2}$ in the direct-growth a-plane GaN. Cathodoluminescence (CL) revealed a four-fold increase in luminous intensity in the overgrown material compared to the wing material. X-ray rocking curves indicated that the films were free of wing tilt within the sensitivity of the measurements. Whereas non-LEO a-plane GaN exhibits basal plane stacking fault and threading dislocation densities of

10^5 cm^{-1} and 10^9 cm^{-2} , respectively, the LEO material was essentially free of extended defects. The basal plane stacking fault and threading dislocation densities in the wing regions were below the sampling limits of $\sim 5 \times 10^6 \text{ cm}^{-2}$ and $3 \times 10^3 \text{ cm}^{-1}$, respectively.

5 FIG. 3 is a cross-sectional scanning electron micrograph (SEM) image of an a-plane GaN stripe grown using the process described above. This stripe has grown through a $5 \text{ }\mu\text{m}$ wide window in the SiO_2 mask and has spread laterally over the SiO_2 mask to a width of approximately $30 \text{ }\mu\text{m}$. If this growth had been continued for a sufficient time, this stripe would have converged with adjacent stripes to form a
10 continuous a-plane GaN surface. The coalesced film will have lower dislocation and stacking fault densities in the overgrown regions due to blocking of dislocations by the mask or bending of dislocations through the transition from vertical to lateral growth. (Note that the chipped edge of the stripe is a cleaving artifact.)

 The masks for the LEO process were prepared by utilizing conventional
15 photolithographic processing and wet etching to $\sim 1300 \text{ }\text{\AA}$ -thick plasma-enhanced chemical vapor deposited SiO_2 layers. A variety of mask designs were investigated, including arrays of circular apertures, parallel stripes oriented along the $[0001]_{\text{GaN}}$ direction, parallel stripes oriented along the $[1\bar{1}00]_{\text{GaN}}$ direction, parallel stripes oriented along the $[1\bar{1}02]_{\text{GaN}}$ direction, and non-parallel stripes in a 'wagon-wheel'
20 pattern. The LEO growth process was carried out in a conventional three-zone horizontal directed-flow HVPE system. (See Reference 9.) Typical vertical growth rates ranged from 16 to $50 \text{ }\mu\text{m}$ per hour at a substrate temperature of $\sim 1040^\circ\text{C}$. A variety of mask geometries yielded coalesced films; in particular the use of masks consisting of periodic arrays of $[1\bar{1}00]$ -oriented stripes allowed full 50 mm -diameter
25 a-plane GaN wafers to be coalesced.

 FIG. 4(a) gives a schematic representation of the $[1\bar{1}00]$ stripe geometry that was used for the samples to be discussed below. Interrupted growths have shown that the (0001) Ga-face wing advances roughly 6 times as rapidly as the $(000\bar{1})$ N-face wing. This ratio indicates that the relative growth rate of the $(000\bar{1})$ wing is

measurably greater in HVPE growth compared to MOCVD growth of GaN, in which the ratio of Ga- to N-face growth is ~ 10 . (See Reference 19.) One benefit of the large difference in lateral growth rates between the $\{0001\}$ faces is that the coalescence front was offset towards the N-face side of the window region, yielding a broad wing region uninterrupted by defective coalescence fronts.

FIG. 4(b) shows a Nomarski™ optical contrast micrograph of a 20 μm -thick coalesced LEO film formed with $[1\bar{1}00]$ -oriented stripes. The faint “fish scale”-like feature on the upper portion of the image demonstrated that the film’s surface is in focus, while the refractive index contrast from the SiO_2 allowed the out-of-focus mask pattern to be observed.

Atomic force microscopy (AFM) was performed to compare the surface morphology in the window and wing regions of the a-plane LEO films. FIG. 4(c) shows a 10 x 10 μm AFM topograph of two coalesced stripes. The window region appeared as the darker band of pitted material, with the coalescence front roughly 1 μm to the left of the window. The Ga-face wing, apparent on the left side of the image, had superior surface quality, exhibiting average pit densities of less than $3 \times 10^6 \text{ cm}^{-2}$, compared to $\sim 10^9 \text{ cm}^{-2}$ in the window regions. The root-mean-square (RMS) roughness of the wing regions was less than 0.9 nm, compared to 1.3 nm in the window regions.

FIG. 5(a) and (b) are cross-sectional SEM images of LEO wafers patterned with a periodic array of $[1\bar{1}00]_{\text{GaN}}$ -oriented SiO_2 stripes. The inclined cross-section in FIG. 5(a) demonstrates the sharply vertical $\{0001\}$ sidewalls that are prevalent for $[1\bar{1}00]$ -oriented stripes throughout lateral growth and immediately preceding coalescence. FIG. 5(b) shows a cross-section view of four coalesced GaN stripes. Only contrast variation at the film-template-interface due to charging effects allows the window and wing regions to be distinguished. FIG. 5(c) is a plan-view SEM image of a coalesced film, again with a mask of SiO_2 stripes oriented along the GaN $[1\bar{1}00]$ direction. The surface was flat and almost featureless, except for a few faint irregular ridges. These ridges manifested themselves in the corresponding CL image

in FIG. 5(d) as dark lines due to scattering. FIG. 5(d) is a CL image of the surface in FIG. 5(c) imaged at the GaN band edge of 365 nm, with lighter shades of grey indicating greater luminous intensity. The window regions in the CL image are apparent as the dark vertical bands. Because of the proximity of the coalescence front to the windows, large, relatively defect-free regions result from the use of $[1\bar{1}00]$ stripes, providing ample surface area for the fabrication of devices. The narrow, dark stripes oriented along the $\langle 0001 \rangle$ direction did not appear to correspond to surface features. The cause of this decreased luminescence is a point of ongoing investigation, though preliminary transmission electron microscopy (TEM) results indicate that clusters of stacking faults lying on the prismatic $\{1\bar{1}00\}$ planes may account for these dark lines.

The structural quality of the a-plane LEO films was characterized by x-ray diffraction (XRD) and TEM. X-ray rocking curves of the $11\bar{2}0$ GaN reflection taken perpendicular to the LEO stripe direction were single-peaked, indicating a lack of measurable tilt in the coalesced films. Narrowing of both on-axis and off-axis reflections was observed in the LEO films compared to planar a-plane GaN films grown directly on r-plane sapphire. (See Reference 19.) Typical full widths at half maximum (FWHM) for the $11\bar{2}0$ and $10\bar{1}0$ reflections were 750 and 1250 arcsec, respectively.

FIGS. 6(a), (b) and (c) show plan-view and cross-sectional TEM images of a LEO film imaged with g vectors of $1\bar{1}00$ and $01\bar{1}0$, respectively. In agreement with observations from AFM and CL, the window regions exhibited high threading dislocation ($\sim 9 \times 10^9 \text{ cm}^{-2}$) and basal plane stacking fault ($\sim 4 \times 10^5 \text{ cm}^{-1}$) densities. In contrast, the Ga-face wing region was essentially free of both dislocations and stacking faults, with densities below the images' sampling limits of $\sim 5 \times 10^6 \text{ cm}^{-2}$ and $\sim 3 \times 10^3 \text{ cm}^{-1}$, respectively. The N-face wing region was also threading dislocation-free, though basal plane stacking faults and Shockley partial dislocations terminating the faults remained prevalent.

The above-described results have demonstrated that substantial reduction in morphological and structural defects in a-plane GaN may be readily achieved by LEO with HVPE. The reduction in threading dislocation density in the overgrown GaN is accompanied by a significant improvement in surface morphology and luminescence compared to non-LEO planar a-plane GaN. Coupling LEO with the comparably high growth rates achievable by HVPE bodes well for the fabrication of high-quality non-polar gallium nitride substrates.

References

The following references are incorporated by reference herein.

1. T. Nishida and N. Kobayashi, Phys. Stat. Sol. (a), 188 (1), 113 (2001). ✓
2. S. Nakamura, G. Fasol, and S. J. Pearton, The Blue Laser Diode. New York: Springer, 2000.
3. L. F. Eastman and U. K. Mishra, IEEE Spectrum, 39 (5), 28 (2002). ✓
4. P. Waltereit, O. Brandt, A. Trampert, H. T. Grahn, J. Menniger, M. Ramsteiner, M. Reiche, and K. H. Ploog, Nature (London), 406, 865 (2000). ✓
5. M.D. Craven, P. Waltereit, F. Wu, J.S. Speck, and S.P. DenBaars, Jpn. J. Appl. Phys., 42 (3A) L235 (2003). ✓
6. H. M. Ng, Appl. Phys. Lett., 80 (23) 4369 (2002). ✓
7. K. Motoki, T. Okahisa, N. Matsumoto, M. Matsushima, H. Kimura, H. Kasai, K. Takemoto, K. Uematsu, T. Hirano, M. Nakayama, S. Nakahata, M. Ueno, D. Hara, Y. Kumagai, A. Koukitu, and H. Seki, Jpn. J. Appl. Phys. Part 2, 40 (2B), L140 (2001). ✓
8. T. Paskova, P.P. Paskov, V. Darakchieva, S. Tungasmita, J. Birch, and B. Monemar, Phys. Stat. Sol. (a) 183 (1) 197 (2001). ✓
9. B. A. Haskell, F. Wu, M. D. Craven, S. Matsuda, P. T. Fini, S. P. DenBaars, J. S. Speck, and S. Nakamura, Submitted for Publication

10. F. Wu, M.D. Craven, S. H. Lim, and J. S. Speck, submitted for publication. ✓
11. T. S. Zheleva, N. Ok-Hyun, M. D. Bremser, and R. F. Davis, Appl. Phys. Lett. 71 (17), 2472 (1997). ✓
- 5 12. N. Ok-Hyun, M. D. Bremser, T. S. Zheleva, and R. F. Davis, Appl. Phys. Lett. 71 (18) 2638 (1997). ✓
13. H. Marchand, J. P. Ibbetson, P. T. Fini, P. Kozodoy, S. Keller, S. DenBaars, J. S. Speck, and U. K. Mishra, MRS Internet J. Nitride Semicond. Res. 3, 3 (1998). ✓
- 10 14. H. Marchand, X. H. Wu, J. P. Ibbetson, P. T. Fini, P. Kozodoy, S. Keller, J. S. Speck, S. P. DenBaars, and U. K. Mishra, Appl. Phys. Lett. 73 (6) 747 (1998). ✓
- 15 15. A. Sakai, H. Sunakawa, A. Kimura, and A. Usui, Appl. Phys. Lett., 76 (4) 442 (2000). ✓
16. O. Parillaud, V. Wagner, H. Bühlmann, and M. Illegems, MRS Internet J. Nitride Semicond. Res., 3, 40 (1998). ✓
17. G. Nataf, B. Beaumont, A. Bouille, S. Haffouz, M. Vaille, and P. Gibart, J. Cryst. Growth, 192, 73 (1998). ✓
18. H. Tsuchiya, K. Sunaba, T. Suemasu, and F. Hasegawa, J. Cryst. Growth, 189/90, 395 (1998). ✓
- 20 19. M. D. Craven, S. H. Lim, F. Wu, J. S. Speck, and S. P. DenBaars, Appl. Phys. Lett., 81 (7) 1201 (2002). ✓

Conclusion

- 25 This concludes the description of the preferred embodiment of the present invention. The following describes some alternative embodiments for accomplishing the present invention.

The preferred embodiment describes a direct one-step lateral overgrowth process in which the a-plane GaN is grown directly off of a patterned sapphire

substrate. Alternative suitable substrate materials, including but not limited to a-plane silicon carbide, may be used in practicing the present invention.

The substrate for the lateral growth process may also consist of a suitable substrate that has been coated with a "template" layer of GaN, AlN, AlGa_N, or other thin film. The use of such templates for subsequent regrowth has been established as a
5 viable technique for the practice of the present invention.

Nucleation layers deposited at either low temperatures or at or above the growth temperature by a variety of growth techniques may also be used for subsequent lateral overgrowth by HVPE using this technique.

10 The preferred embodiment utilizes a carrier gas containing predominantly hydrogen. While a fraction of hydrogen must be present over the growth surface, other gases may be present in the carrier gas stream, including (but not limited to) nitrogen, argon, or helium.

Additionally, a variety of mask materials, mask deposition techniques, and
15 patterning methods may be used in the practice of this invention without significantly altering the results of the invention. Indeed, both dielectric materials such as silicon dioxide and silicon nitride, and metallic materials such as titanium, can be utilized as masks in the practice of this invention.

Another alternative approach is to etch a pattern into the substrate material
20 rather than deposit a patterned mask on the substrate by, for example, reactive ion etching. In such an approach, the depth and width of the trenches in the substrate, as well as the system pressure and specifically ammonia partial pressure, should be chosen such that the film growing laterally from the unetched plateaus coalesce before the GaN growing from the bottom of the trenches reaches the top of the trenches. This
25 technique, known as cantilever epitaxy, has been demonstrated for polar c-plane GaN growth, and should be compatible with the present invention.

The geometry of the mask pattern described herein significantly affects the behavior of the laterally growing film. Masks containing stripes with various orientations relative to the substrate have been used, in addition to apertures of

various sizes, shapes, and spacings. While the growth behavior from each shape opening differs, it has been shown that the mask geometry does not fundamentally alter the practice of this invention. Thus, any mask containing some regions where GaN nucleation is preferred and some regions where GaN nucleation is discouraged is
5 acceptable, irrespective of geometry.

Reactor geometry and design may affect the practice of the present invention, as discussed further in the co-pending and commonly-assigned International Application No. PCT/US03/-----, entitled "GROWTH OF PLANAR, NON-POLAR A-PLANE GALLIUM NITRIDE BY HYDRIDE VAPOR PHASE EPITAXY," filed
10 on same date herewith, by Benjamin A. Haskell, Paul T. Fini, Shigemasa Matsuda, Michael D. Craven, Steven P. DenBaars, James S. Speck, and Shuji Nakamura, attorneys docket number 30794.94-WO-U1, which application claims priority to co-pending and commonly-assigned United States Provisional Patent Application Serial No. 60/433,844, entitled "TECHNIQUE FOR THE GROWTH OF PLANAR,
15 NON-POLAR A-PLANE GALLIUM NITRIDE BY HYDRIDE VAPOR PHASE EPITAXY," filed on December 16, 2002, by Benjamin A. Haskell, Paul T. Fini, Shigemasa Matsuda, Michael D. Craven, Steven P. DenBaars, James S. Speck, and Shuji Nakamura, attorneys docket number 30794.94-US-P1; and United States Provisional Patent Application Serial No. 60/433,843, entitled "GROWTH OF
20 REDUCED DISLOCATION DENSITY NON-POLAR GALLIUM NITRIDE BY HYDRIDE VAPOR PHASE EPITAXY," filed on December 16, 2002, by Benjamin A. Haskell, Michael D. Craven, Paul T. Fini, Steven P. DenBaars, James S. Speck, and Shuji Nakamura, attorneys docket number 30794.93-US-P1; which applications are incorporated by reference herein. However, it should be mentioned that the growth
25 parameters required for the successful lateral overgrowth of non-polar GaN may vary from reactor to reactor. Such variations do not fundamentally alter the general practice of this invention.

Additionally, while in general it is desirable to continue the lateral growth process to the point of film coalescence, coalescence is not a requirement of the

present invention. Indeed, it is envisioned that there may be a number of applications in which uncoalesced laterally-overgrown non-polar GaN stripes or pillars would be highly desirable. Therefore, the present invention applies to both coalesced and uncoalesced laterally overgrown non-polar GaN films.

5 Finally, the processes described herein may be scaled for multiple wafer growth. Specifically, the present invention may be practiced through the growth of films on multiple wafers simultaneously.

 In summary, the present invention describes defect reduction in non-polar GaN grown by HVPE, thereby significantly improving film quality and allowing
10 fabrication of enhanced GaN substrate layers for subsequent non-polar device fabrication.

 The foregoing description of one or more embodiments of the invention has been presented for the purposes of illustration and description. It is not intended to be exhaustive or to limit the invention to the precise form disclosed. Many modifications
15 and variations are possible in light of the above teaching. It is intended that the scope of the invention be limited not by this detailed description, but rather by the claims appended hereto.

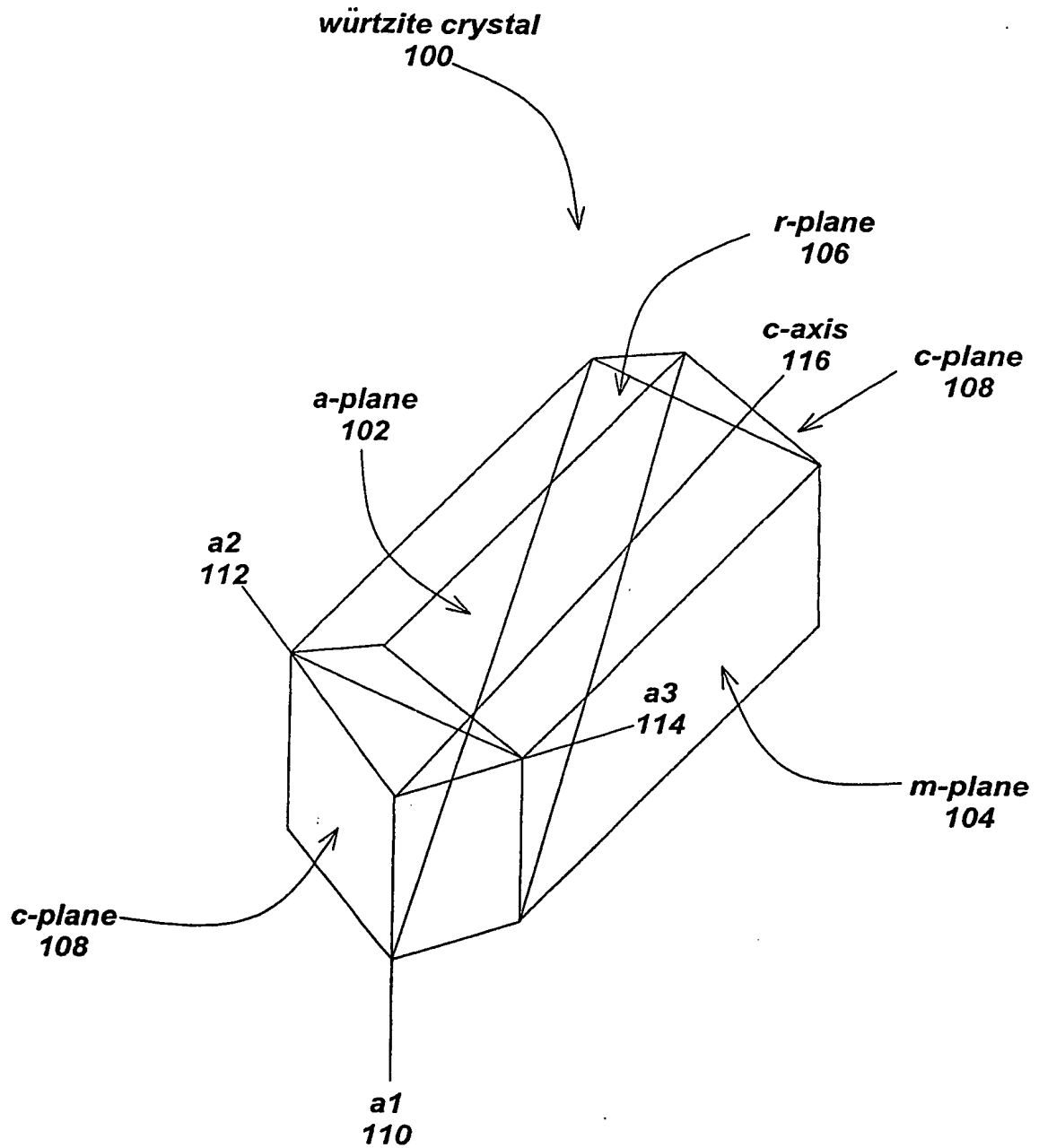
WHAT IS CLAIMED IS:

1. A method of performing a lateral epitaxial overgrowth of a planar, non-polar, a-plane gallium nitride (GaN) film, comprising:
 - (a) patterning a mask deposited on a substrate; and
 - 5 (b) performing a lateral epitaxial overgrowth of the GaN film off the substrate using hydride vapor phase epitaxy, wherein the GaN film nucleates only on portions of the substrate not covered by the patterned mask, the GaN film grows vertically through openings in the patterned mask, and the GaN film then spreads laterally above the patterned mask and across the substrate's surface.
- 10 2. The method of claim 1, wherein the lateral epitaxial overgrowth utilizes growth pressures of approximately atmospheric pressure (760 Torr) or below, and a carrier gas containing a fraction of hydrogen.
- 15 3. The method of claim 1, wherein the growth pressure is less than 300 Torr.
4. The method of claim 1, wherein the growth pressure ranges from 5 to 100 Torr.
- 20 5. The method of claim 1, wherein the carrier gas is predominantly hydrogen.
6. The method of claim 1, wherein the carrier gas comprises a mixture of 25 hydrogen and nitrogen, argon, or helium.
7. The method of claim 1, wherein the lateral epitaxial overgrowth reduces threading dislocation densities in the GaN film.

8. The method of claim 1, wherein the substrate comprises sapphire.
9. The method of claim 1, wherein the patterned mask is comprised of a metallic material.
- 5 10. The method of claim 1, wherein the patterned mask is comprised of a dielectric material.
- 10 11. The method of claim 1, wherein the patterned mask is a silicon dioxide (SiO_2) mask containing apertures or stripes allowing access to the substrate underlying the mask.
12. The method of claim 1, wherein the patterning step comprises:
depositing a silicon dioxide (SiO_2) film on the substrate;
15 patterning a photoresist layer on the silicon dioxide film;
etching away any portions of the silicon dioxide film exposed by the patterned photoresist layer;
removing remaining portions of the photoresist layer; and
cleaning the substrate.
- 20 13. The method of claim 1, wherein the substrate is coated with a template layer of GaN, aluminum nitride (AlN), aluminum gallium nitride (AlGaN), or other thin film.
- 25 14. The method of claim 1, wherein the substrate is a free-standing α -plane GaN, α -plane aluminum nitride (AlN), or α -plane aluminum gallium nitride (AlGaN) wafer.

15. The method of claim 1, wherein the substrate is coated with a nucleation layer deposited at either low temperatures or at the growth temperature.
16. A free-standing *a*-plane GaN film or substrate manufactured using the
5 method of claim 1.
17. A device manufactured using the method of claim 1.
18. The device of claim 17, wherein the device is a laser diode, light-
10 emitting diode or transistor.
19. A lateral epitaxial overgrowth of a planar, non-polar, *a*-plane gallium nitride (GaN) film off a substrate, wherein the lateral epitaxial overgrowth is created using a process comprising:
- 15 (a) patterning a dielectric mask deposited on a substrate; and
(b) performing a lateral epitaxial overgrowth of the GaN film off the substrate using hydride vapor phase epitaxy, wherein the GaN film nucleates only on portions of the substrate exposed by the patterned dielectric mask, the GaN film grows vertically through openings in the patterned dielectric mask, and the GaN film then
20 spreads laterally above the patterned dielectric mask and across the substrate's surface.

1/6

**FIG. 1**

2/6

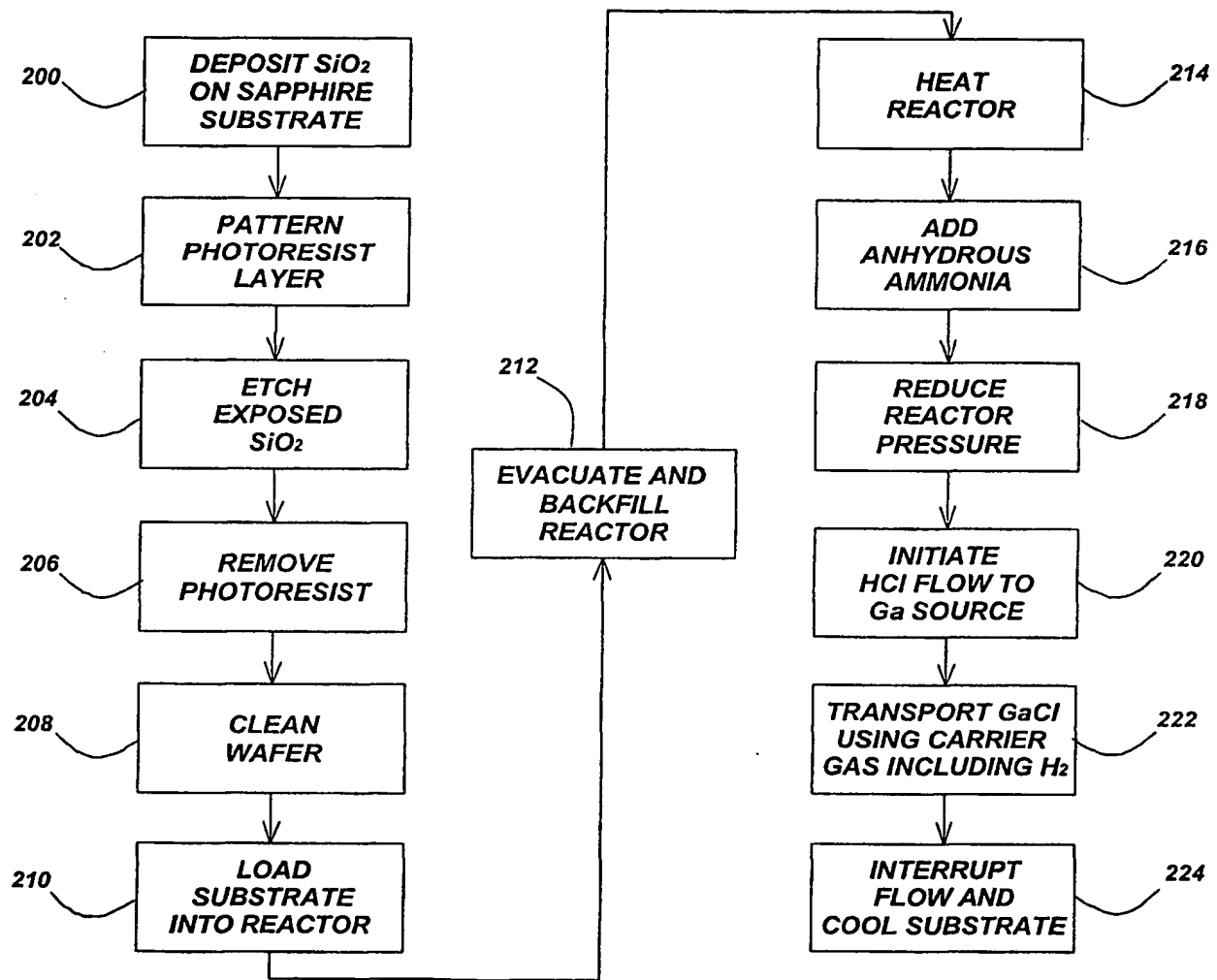


FIG. 2

3/6

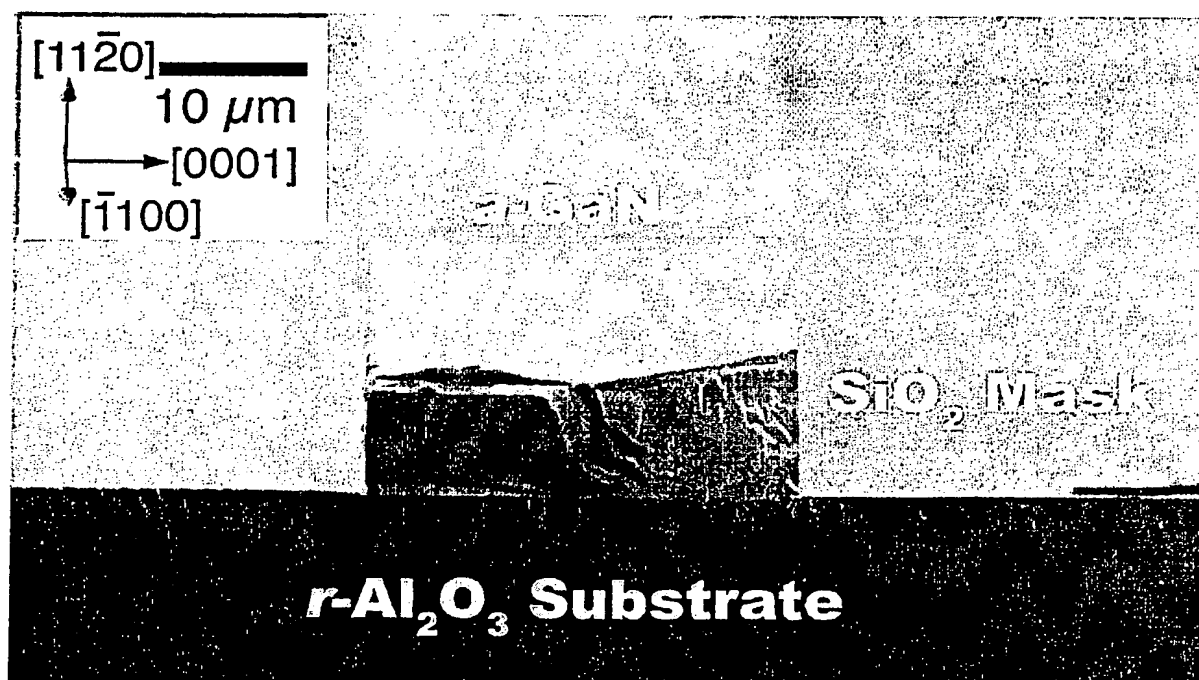


FIG. 3

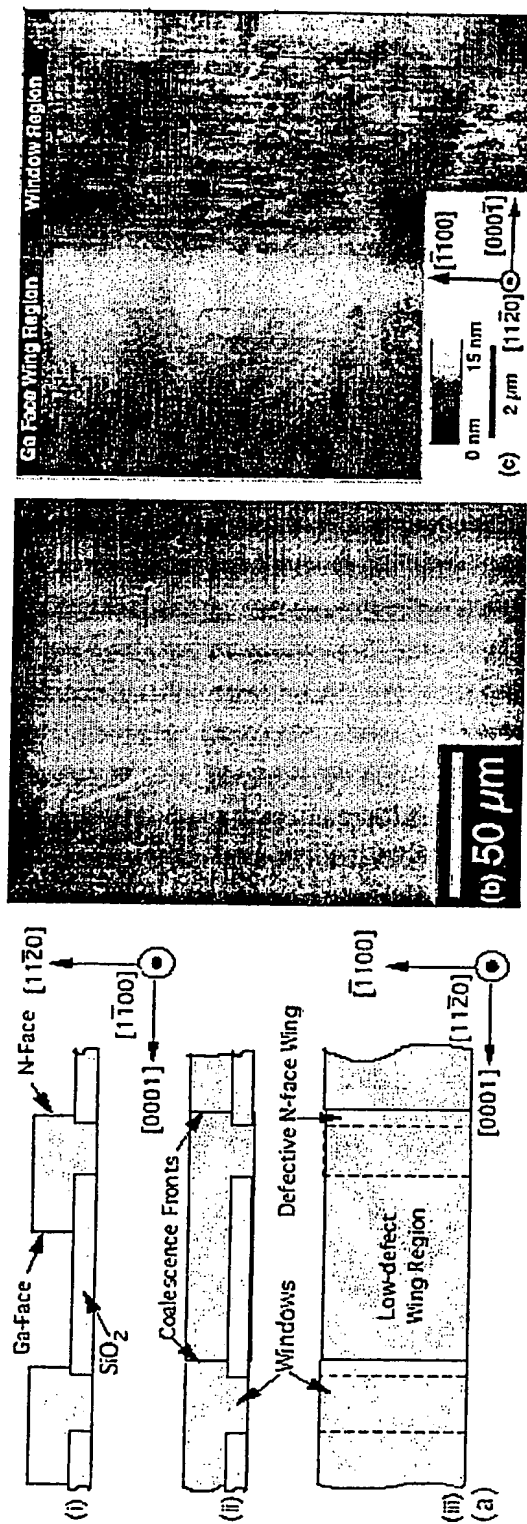


FIG. 4

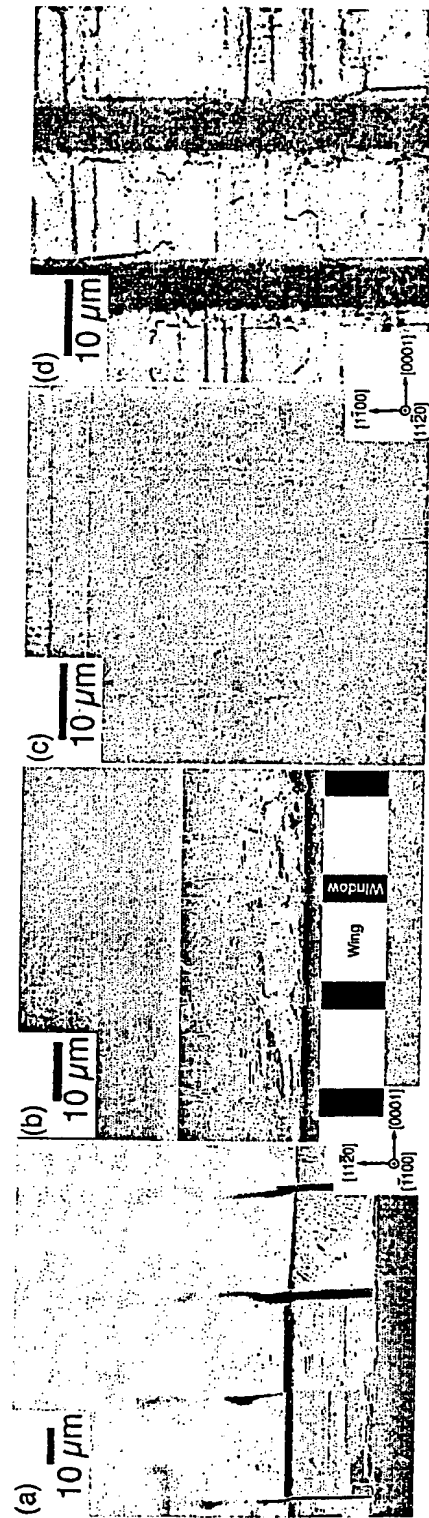


FIG. 5

6/6

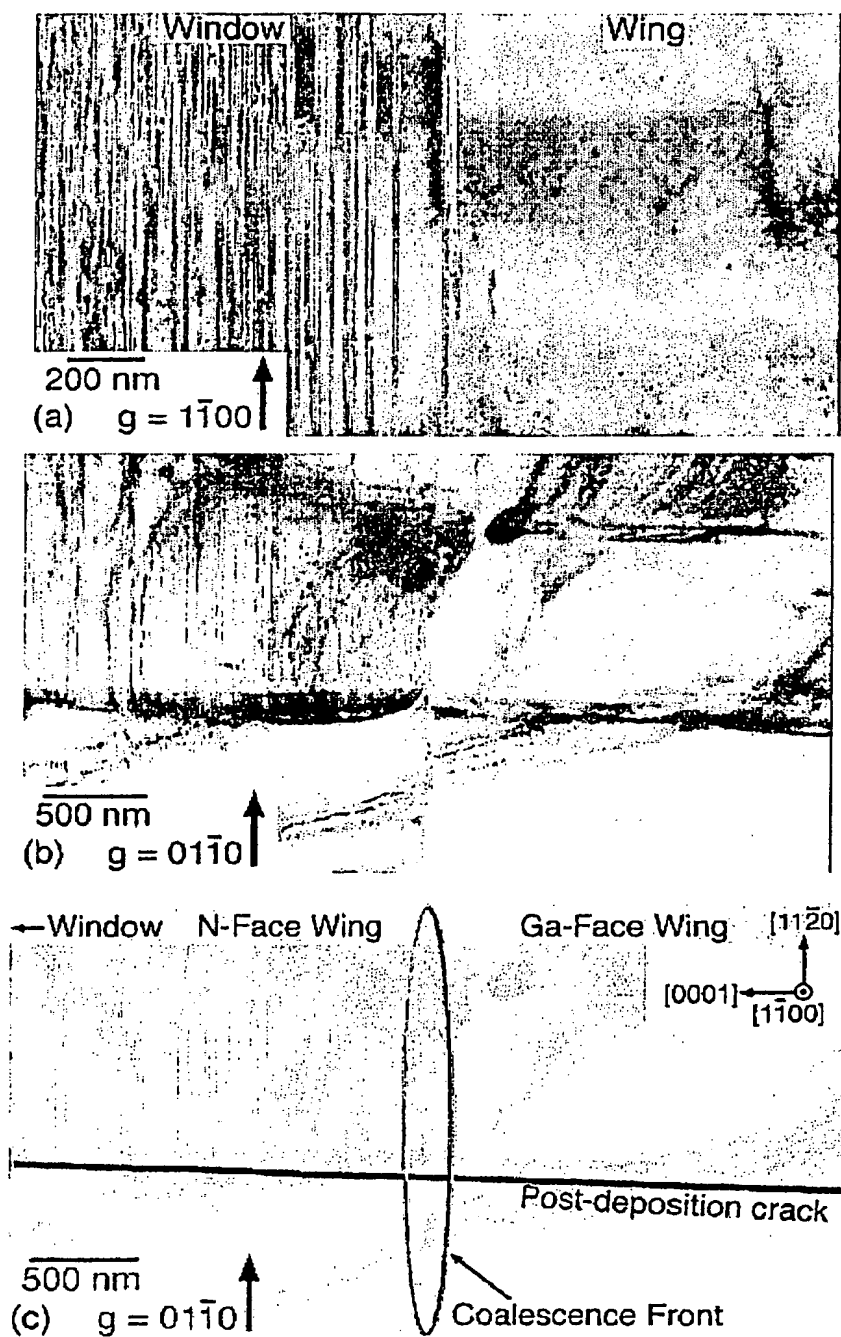


FIG. 6

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US03/21918

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : H01L 21/00

US CL : 438/46, 481

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 438/46, 479, 481, 483, 484

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
IEEEExplore, Japanese Journal of Applied Physics

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 6,413,627 B1 (MOTOKI et al) 02 July 2002 (02.07.2002), see entire document.	1-19
A,P	US 6,582,986 B2 (KONG et al) 24 June 2003 (24.06.2003), see entire document.	1-19
A,P	US 6,602,763 B2 (DAVIS et al) 05 August 2003 (05.08.2003), see entire document.	1-19
A,E	US 6,645,295 B1 (KOIKE et al) 11 November 2003 (11.11.2003), see entire document.	1-19
A	WANG et al, Crystal Tilting in the Epitaxial Laterally GaN Films on Sapphire Substrate by Hydride Vapor Phase Epitaxy. Solid-State and Integrated-Circuit Technology Proceedings 6th International Conference, October 2001, Vol. 2, pages 1198-1201.	1-19
A,P	MARUSKA et al, Development of 50 mm Diameter Non-Polar Gallium Nitride Substrates for Device Applications. International Conference on Indium Phosphide and Related Materials, 16 May 2003 (16.05.2003), pages 567-570.	1-19

☐ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T"

later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X"

document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y"

document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&"

document member of the same patent family

Date of the actual completion of the international search

02 February 2004 (02.02.2004)

Date of mailing of the international search report

15 APR 2004

Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US
Commissioner for Patents
P.O. Box 1450
Alexandria, Virginia 22313-1450

Facsimile No. (703) 305-3230

Authorized officer

Beth Owens

Telephone No. (571) 272-1882

Rene P. Smith

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☐ **FADED TEXT OR DRAWING**
- ☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☐ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☒ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.